

# Decreasing build-up of inorganic incrustations on fabrics and washing machine components - by addn. to washing cycle of co-builder based on carbohydrate or its deriv having specified dextrose equiv.

**Patent Number : EP-703292**

*International patents classification : C11D-000/00 C11D-003/22 C11D-003/37 C11D-007/26 C11D-007/38 C11D-007/44 C11D-011/00*

**• Abstract :**

EP-703292 A Decreasing build-up of inorganic incrustations on fabrics and washing machine components during multiple washing cycles, comprises adding to washing cycle, a co-builder based on a carbohydrate or its deriv having a dextrose equiv. (DE) of 0.5-20.  
Also claimed is a detergent and/or anti-incrustation compsn. contg. the co-builder based on the carbohydrate or its deriv.  
Carbohydrate or its deriv is maltodextrin having DE of 8-17. Co-builder is added directly to washing bath in amt. of 1-40 (esp 2-20)g/washing cycle or is incorporated in detergent compsn. in amt. of 0.5-20 (esp. 1-10)% expressed as 100% dry substance of detergent and/or anti-incrustation compsn.  
Detergent and/or anti-incrustation compsn. contains zeolite and inorganic persalt.  
ADVANTAGE - Co-builder shows a high efficiency in reducing incrustations build-up when combined with detergents esp. zeolite based detergents.  
Furthermore, the co-builders are cheap and biodegradable and are efficacious in the presence of inorganic persalts. (Dwg.0/0)

**• Publication data :**

Patent Family : EP-703292 A1 19960327 DW1996-17 C11D-003/22 Eng 4p \* AP: 1995EP-0306663 19950921 DSR: AT BE CH DE DK ES FR GB GR IE IT LI NL PT SE  
CA2158714 A 19960323 DW1996-27 C11D-007/26 AP:  
1995CA-2158714 19950920  
FI9504506 A 19960323 DW1996-35 C11D-000/00 AP: 1995FI-0004506 19950922  
JP08176593 A 19960709 DW1996-37 C11D-003/22 3p AP:  
1995JP-0243433 19950921  
MX9504068 A1 19970201 DW1998-18 C11D-003/37 AP:  
1995MX-0004068 19950922  
EP-703292 B1 20010418 DW2001-23 C11D-003/22 Eng AP:  
1995EP-0306663 19950921 DSR: AT BE CH DE DK ES FR GB GR IE IT LI NL PT SE  
DE69520720 E 20010523 DW2001-37 C11D-003/22 FD: Based on EP-703292 AP: 1995DE-6020720 19950921; 1995EP-0306663 19950921  
ES2155500 T3 20010516 DW2001-38 C11D-003/22 FD: Based on EP-703292 AP: 1995EP-0306663 19950921  
Priority n° : 1994GB-0019091 19940922  
Covered countries : 19  
Publications count : 8  
Cited patents : EP-472042; EP-618286; JP52059605; US3022343 01Jnl.Ref

**• Patentee & Inventor(s) :**

Patent assignee : (CERE-) CERESTAR HOLDING BV  
Inventor(s) : BECK RHF

**• Accession codes :**

Accession N° : 1996-161644 [17]  
Sec. Acc. n° CPI : C1996-051236

**• Derwent codes :**

Manual code : CPI: D11-A D11-B03 D11-B10 D11-D01  
Derwent Classes : D25 E13

**• Update codes :**

Basic update code :1996-17  
Equiv. update code :1996-27; 1996-35; 1996-37; 1998-18; 2001-23; 2001-37; 2001-38

Others :  
UE4

2001-04; 2001-07





Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 0 703 292 B1**

**EUROPEAN PATENT SPECIFICATION**

(12)

(45) Date of publication and mention  
of the grant of the patent:  
18.04.2001 **Bulletin 2001/16**

(51) Int Cl.<sup>7</sup>: **C11D 3/22, C11D 7/44,  
C11D 11/00**

(21) Application number: **95306663.6**

(22) Date of filing: **21.09.1995**

(54) **Process for decreasing the build up of inorganic incrustations on textiles and detergent composition used in such a process**

Verfahren zur Verringerung der Ausbildung von Inkrustationen auf Textilien und Waschmittel für das Verfahren

Méthode pour réduire la formation de dépôt d'incrustations inorganiques sur les textiles et composition détergente utilisée dans ce procédé

(84) Designated Contracting States:  
**AT BE CH DE DK ES FR GB GR IE IT LI NL PT SE**

(30) Priority: **22.09.1994 GB 9419091**

(43) Date of publication of application:  
**27.03.1996 Bulletin 1996/13**

(73) Proprietor: **CERESTAR HOLDING BV  
NL-4550 AA Sas Van Gent (NL)**

(72) Inventor: **Beck, Roland Herwig Friedrich, Dr.  
B-3078 Everberg (BE)**

(74) Representative: **Wilkinson, Stephen John  
Stevens, Hewlett & Perkins  
1 St. Augustine's Place  
Bristol BS1 4UD (GB)**

(56) References cited:  
**EP-A- 0 472 042 EP-A- 0 618 286  
US-A- 3 022 343**

• **DATABASE WPI Section Ch, Week 2677 Derwent  
Publications Ltd., London, GB; Class A97, AN  
77-45788Y & JP-A-52 059 605 ( KAO SOAP KK) ,  
17 May 1977**

**EP 0 703 292 B1**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

## Description

[0001] The present invention relates to a process for decreasing the build-up of inorganic incrustations on fabrics caused by water hardness and repeated washing cycles with detergent compositions.

[0002] More particularly, the present invention relates to a process for decreasing the build-up of inorganic incrustations wherein a co-builder is added to the washing cycle, and to detergent and/or anti-incrustation compositions containing said co-builder.

[0003] It is well known that detergents contain builders in order to support detergent action and to eliminate calcium and magnesium ions (hardness ions), which arise partly from the water and sometimes also from soil and fabrics.

[0004] In case of multiple washing cycles the washing performance is significantly reduced because of the build up of inorganic incrustations on fabrics and on washing machine components. Such build up of inorganic incrustations on fabrics decreases the flexibility of fibres and consequently shortens the fabric life, in addition to greying the tissue.

[0005] A well known builder is sodium tripolyphosphate which has excellent properties in the washing process even at low concentrations. Despite its many advantageous properties however, it causes serious ecological problems, namely eutrophication of stationary or slowly flowing surface waters leading to extreme algal growth which adversely influences marine organisms. As a result, the use of phosphate free detergents is of great importance.

[0006] Some substitutes of phosphate builders such as zeolites have been adopted. However, zeolites alone in water softening have poor efficiency. Therefore, good anti-incrustation effects are achieved only in the presence of auxiliary compounds called co-builders.

[0007] The most widely used co-builders are synthetic polymers and/or co-polymers of olefinic mono- or dicarboxylic acids such as acrylic and maleic acid and copolymers of said monomers with other allylic or vinylic monomers. A common characteristic of these polymeric materials is their minimal biodegradability which leads to ecological problems.

[0008] There are known other non-polymeric co-builders, such as EDTA (ethylenediaminetetraacetic acid sodium salt), NTA (nitrilotriacetic acid sodium salt) and phosphonates. As with the polymeric co-builders these substances too are non-biodegradable.

[0009] It is therefore an object of the present invention to provide a process for decreasing the build-up of inorganic incrustations on fabrics and on washing machine components by using co-builders which are very efficient in reducing incrustation build up during washing cycles and which are cheap and biodegradable.

[0010] Another object of the present invention is to provide detergent and/or anti-incrustation compositions containing said biodegradable co-builders.

[0011] It has now surprisingly been found that certain carbohydrates show a high efficiency in reducing incrustation build up when combined with detergents, particularly with zeolite-based detergents.

[0012] In EP-A-0618286 there is described a co-builder based upon a non-reducing carbohydrate or a non-reducing carbohydrate derivative. Preferred among the non-reducing carbohydrate derivatives are certain sugar alcohols exemplified by maltitol and, especially, by mannitol. It has now been found however that the carbohydrate or carbohydrate derivative need not be fully non-reducing but that some reducing activity is tolerable and that certain compounds showing such activity are as effective co-builders as the sugar alcohols referred to above.

[0013] EP-A-0472042 discloses calcium-sequestering agents based on oxidised carbohydrates, a method for their preparation, and their use as builders or detergents. The document also relates to the sequestering capacity of oxidised glucosidic oligomers. The oxidation is performed with hypochlorite or periodate, both giving highly oxidised products. JP-A-52059605 (Abstract) describes as a builder component a carboxymethylated hydrolysate of starch, cellulose or hemicellulose, in which the average degree of substitution by carboxymethyl groups for three hydroxyl groups in a structural unit is 1.5 to 3.0. The products contain a high density of carboxymethyl groups.

[0014] In accordance with one aspect of the present invention therefore there is provided a process for decreasing the build-up of inorganic incrustations on fabrics and on washing machine components during multiple washing cycles with detergent compositions characterised by the addition to the washing cycle of a co-builder based on a carbohydrate or carbohydrate derivative having a DE of 0.5 to 20 inclusive. The carbohydrate or carbohydrate derivative is selected from polydextrose, partially degraded inulin and maltodextrin.

[0015] A range of carbohydrates or carbohydrate derivatives having a DE of 0.5 to 20 inclusive may be used in the process of the invention eg. polydextrose or partially degraded inulin but preferably the carbohydrate or carbohydrate derivative is a maltodextrin having a DE of 0.5 to 20 inclusive, particularly a DE of 8 to 17 inclusive.

[0016] "DE" or dextrose equivalent is a measure of the reducing activity of a carbohydrate measured by comparison with dextrose which has a DE of 100.

[0017] The co-builders based on such carbohydrates and carbohydrate derivatives having a DE of 0.5 to 20 inclusive can be incorporated into the detergent compositions or added as such directly to the washing bath.

[0018] In accordance with another aspect of the present invention, there are provided detergent and/or anti-incrustation compositions containing the hereinbefore defined co-builders. These compositions may also contain other con-

ventional components such as anionic, non-ionic, cationic or amphoteric surfactants, alkali metal salts (e.g. sodium carbonate, sodium silicate), neutral salts (e.g. sodium sulphate), zeolites, bleaching agents, bleaching activators and other minor ingredients.

[0019] In accordance with one preferred embodiment of the present invention the novel co-builders are used in combination with zeolite-based detergents.

[0020] The co-builders used according to the present invention are particularly efficacious in the presence of inorganic persalts, such as sodium perborate tetrahydrate or monohydrate.

[0021] The amount of the co-builders used in the process can vary from 1 g/washing cycle to 40 g/washing cycle, and preferably from 2 g/washing cycle to 20 g/washing cycle. This amount is achieved by a range of from 0.5 % to 20 % and preferably by a range of from 1 % to 10 %, expressed as 100 % dry substance of co-builder in the detergent or anti-incrustation compositions.

[0022] The co-builders used according to the present invention are naturally derived, biodegradable compounds. In combination with detergents they reduce the build up of inorganic incrustations on fabrics and on washing machine components. Such activity is more significant at high temperatures e.g. at 90°C.

[0023] The present invention is disclosed in still further detail in the following Example, which is supplied for purely illustrative and not limiting purposes.

#### Example

[0024] The co-builder activities of the following compositions were evaluated on a laboratory scale using the so-called "Hampshire" test which measures the  $\text{Ca}^{++}$  sequestering capacity of the composition. The test was carried out as follows:

1 gram of the substance under test is dissolved in 100 ml of demineralised water, the solution filtered and the filtrate made up to 100 ml with demineralised water. 10 ml of a 2 % by weight aqueous solution of sodium carbonate is then added, the pH adjusted to 11 with sodium hydroxide solution (0.1 N or more concentrated for a large pH adjustment) and the temperature regulated at 20°C. The solution is then titrated with a calcium acetate solution (39.59 g/l) at a rate of 1 ml/min until a permanent turbidity becomes apparent. The quantity of  $\text{Ca}^{++}$  in the calcium acetate solution, determined by a preliminary titration with EDTA, is 10.03 mg  $\text{Ca}^{++}$ /ml.

[0025] The results of the determinations in mg  $\text{Ca}^{++}$ /g of test substance were as follows :

Substance	Solution with borax (2g/50 ml)	Solution without borax
Maltodextrin (DE = 12)	40.7	9.7
Mannitol (comparitive)	46.9	7.9
Maltitol (comparitive)	47.8	9.2

#### Claims

1. A process for decreasing the build up of inorganic incrustations on fabrics and on washing machine components during multiple washing cycles characterized by the addition to the washing cycle of a co-builder based on a carbohydrate or carbohydrate derivative having a DE of 0.5 to 20 inclusive, wherein the carbohydrate or carbohydrate derivative is selected from polydextrose, partially degraded inulin and maltodextrin.
2. The process according to Claim 1, characterized in that the carbohydrate or carbohydrate derivative is a maltodextrin.
3. The process according to Claim 2 characterized in that the maltodextrin has a DE of 8 to 17 inclusive.
4. The process according to Claim 1, characterized in that the co-builder as such is added directly to the washing bath.
5. The process according to Claim 4, characterized in that the co-builder is added in amount ranging from 1 g/washing cycle to 40 g/washing cycle, preferably from 2 g/washing cycle to 20 g/washing cycle.
6. The process according to Claim 1, characterized in that the co-builder is incorporated in the detergent composition.
7. Detergent and/or anti-incrustation composition containing a co-builder based on a carbohydrate or carbohydrate derivative having a DE of 0.5 to 20, wherein the carbohydrate or carbohydrate derivative is selected from polydex-

trose, partially degraded inulin and maltodextrin.

8. Detergent and/or anti-incrustation composition according to Claim 7, characterized in that it contains a zeolite
- 5 9. Detergent and/or anti-incrustation composition according to Claim 7, characterized in that it contains the co-builder in an amount ranging from 0.5 % to 20 %, preferably from 1 % to 10 %, expressed as 100 % dry substance of the detergent or anti-incrustation composition.
- 10 10. Detergent and/or anti-incrustation composition according to Claim 7, characterized in that it contains an inorganic persalt.

#### Patentansprüche

- 15 1. Verfahren zur Verringerung der Ausbildung von anorganischen Inkrustationen auf Textilien und auf Waschmaschinenteilen während mehrerer Waschgänge, gekennzeichnet durch die Zugabe eines Cobuilders, der auf einem Kohlenhydrat oder Kohlenhydratderivat mit einem DE-Wert von 0,5 bis einschließlich 20 basiert, zu dem Waschgang, wobei das Kohlenhydrat oder Kohlenhydratderivat aus Polydextrose, teilweise abgebautem Inulin und Maltodextrin ausgewählt ist.
- 20 2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass das Kohlenhydrat oder Kohlenhydratderivat ein Maltodextrin ist.
- 25 3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, dass das Maltodextrin einen DE-Wert von 8 bis einschließlich 17 aufweist.
4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass der Cobuilder als solcher direkt zu der Waschflotte gegeben wird.
- 30 5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, dass der Cobuilder in einer Menge im Bereich von 1 g/Waschgang bis 40 g/Waschgang, vorzugsweise 2 g/Waschgang bis 20 g/Waschgang, zugegeben wird.
6. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass der Cobuilder in das Waschmittel eingearbeitet wird.
- 35 7. Waschmittel und/oder Antiinkrustationszusammensetzung, enthaltend einen Cobuilder, der auf einem Kohlenhydrat oder Kohlenhydratderivat mit einem DE-Wert von 0,5 bis 20 basiert, wobei das Kohlenhydrat oder Kohlenhydratderivat aus Polydextrose, teilweise abgebautem Inulin und Maltodextrin ausgewählt ist.
- 40 8. Waschmittel und/oder Antiinkrustationszusammensetzung nach Anspruch 7, dadurch gekennzeichnet, dass es einen Zeolith enthält.
9. Waschmittel und/oder Antiinkrustationszusammensetzung nach Anspruch 7, dadurch gekennzeichnet, dass es/sie den Cobuilder in einer Menge von 0,5% bis 20%, bevorzugt von 1% bis 10% enthält, ausgedrückt als 100% Trockensubstanz des Waschmittels oder der Antiinkrustationszusammensetzung.
- 45 10. Waschmittel und/oder Antiinkrustationszusammensetzung nach Anspruch 7, dadurch gekennzeichnet, dass es/sie ein anorganisches Persalz enthält.

#### 50 Revendications

1. Procédé pour diminuer l'accumulation d'incrustations inorganiques sur des tissus et sur des composants d'un lave linge pendant de multiples cycles de lavage, caractérisé par l'ajout lors du cycle de lavage d'un co-adjuvant basé sur un hydrate de carbone ou un dérivé d'hydrate de carbone ayant un DE de 0,5 à 20 inclus, dans lequel l'hydrate de carbone ou le dérivé d'hydrate de carbone est sélectionné parmi du polydextrose, de l'inuline partiellement dégradée et de la maltodextrine.
- 55 2. Procédé selon la revendication 1, caractérisé en ce que l'hydrate de carbone ou le dérivé d'hydrate de carbone

est une maltodextrine.

3. Procédé selon la revendication 2, caractérisé en ce que la maltodextrine a un DE de 8 à 17 inclus.
- 5 4. Procédé selon la revendication 1, caractérisé en ce que le co-adjuvant est ajouté tel quel directement au bain de lavage.
5. Procédé selon la revendication 4, caractérisé en ce que le co-adjuvant est ajouté selon une quantité se trouvant dans la plage allant de 1 g/cycle de lavage à 40 g/cycle de lavage, de préférence de 2 g/cycle de lavage à 20 g/  
10 cycle de lavage.
6. Procédé selon la revendication 1, caractérisé en ce que le co-adjuvant est incorporé dans la composition détergente.
- 15 7. Composition détergente et/ou anti-incrustation contenant un co-adjuvant basé sur un hydrate de carbone ou un dérivé d'hydrate de carbone ayant un DE de 0,5 à 20, dans laquelle l'hydrate de carbone ou le dérivé d'hydrate de carbone est sélectionné parmi du polydextrose, de l'inuline partiellement dégradée et de la maltodextrine.
- 20 8. Composition détergente et/ou anti-incrustation selon la revendication 7, caractérisée en ce qu'elle contient une zéolite.
9. Composition détergente et/ou anti-incrustation selon la revendication 7, caractérisée en ce qu'elle contient le co-adjuvant en quantité de 0,5% à 20%, de préférence de 1% à 10% sous la forme de 100% de substance sèche de la composition détergente et/ou anti-incrustation.
- 25 10. Composition détergente et/ou anti-incrustation selon la revendication 7, caractérisée en ce qu'elle contient un persel inorganique.

30

35

40

45

50

55

